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# In situ catalytic pyrolysis of lignocellulose using alkali-modified amorphous silica alumina

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## HIGHLIGHTS

- ▶ Alkali-modified amorphous silical alumina (ASA) catalysts are effective for bio-oil upgrading.
- ▶ Among the alkalis tested, Cs/ASA catalyst is promising for: Cracking of lignin fraction of biomass.
- ▶ Deoxygenating of substituted phenols.
- ▶ Producing hydrocarbons.

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## ABSTRACT

Canadian pinewood was pyrolyzed at 450 °C in an Infrared oven and the pyrolysis vapors were converted by passing through a catalyst bed at 450 °C. The catalysts studied were amorphous silica alumina (ASA) containing alkali metal or alkaline earth metal species including Na, K, Cs, Mg and Ca. The catalysts effectiveness to reduce the bio-oil oxygen content, to enhance the bio-oil energy density and to change the liquid and gas product distribution were evaluated using different techniques including gravimetric analysis, elemental analysis, Karl–Fischer titration, GC/MS and micro-GC analysis. According to the results K/ASA found to be the most effective catalysts for conversion of hollocellulose (hemicellulose and cellulose)-derived vapors of pinewood while Cs/ASA catalyst was the most effective catalyst for conversion of lignin-derived vapors and production of hydrocarbons.

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## 1. Introduction

Depletion of fossil resources, increasing demand for petroleum fuels and concerns over global warming have created interest in renewable feedstock's. Biomass is a renewable source of energy, consists mainly of carbon, hydrogen and oxygen and has a nominal composition of C<sub>8</sub>H<sub>4</sub>O<sub>6</sub>. It also contains certain amounts of alkali and alkali earth metals, depending on the biomass source (Fassinou et al., 2011). Compared to fossil fuel resources biomass has lower H/C ratio and higher O/C ratio and as a consequence the energy density is lower than crude oil (16 vs. 44 MJ kg<sup>−1</sup> for crude oil) (Mortensen et al., 2011). Liquefaction of solid biomass is proposed to be advantageous for reasons of logistics, transport and processing

issues. The product of liquefaction is an intermediate energy carrier and can be used as “bio-crude oil” for refineries (Kersten et al., 2007). The most used liquefaction process is fast pyrolysis, a process in which biomass is liquefied by rapid heating to temperatures around 450–550 °C in the absence of oxygen. The liquid product is a complex mixture of organic components and water and is named “bio-liquid”, “bio-oil” or “pyrolysis oil”. It cannot be directly used as a transportation fuel because it (i) is very viscous due to the presence of large molecules (up to 1500 D), (ii) corrosive due to the presence of organic acids, (iii) thermally unstable owing to a large content of reactive components and (iv) has a very low heating value (19 MJ kg<sup>−1</sup>) due to its low hydrogen and high oxygen content.

Accordingly, the development of technologies to reduce the product acidity and to increase stability and energy content of bio-oil is essential. One of the options to achieve this is by reducing the oxygen content of bio-oil. Oxygen removal can be achieved by (i) hydro-deoxygenation (HDO) using (standard) hydrotreating catalysts around 300–500 °C and high hydrogen pressures (Ardiyanti

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et al., 2011), and (ii) deoxygenation over solid acid catalysts at 400–500 °C and atmospheric pressure. HDO process is expensive due to the high prices and low availability of H<sub>2</sub> (Bridgwater, 2012; Huber et al., 2006).

During deoxygenation, oxygen is removed as H<sub>2</sub>O, CO and CO<sub>2</sub> (Zhang et al., 2011). Selective deoxygenation via CO<sub>2</sub> instead of H<sub>2</sub>O, is advantageous because it minimizes loss of hydrogen and maximizes oxygen removal with minimal carbon loss and thus allows to maintain high H/C ratio and low O/C ratio for the bio-oil. Fig. 1 shows this advantage for the selective deoxygenation for glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>). Deoxygenation as H<sub>2</sub>O is least interesting as it lowers the H/C ratio of the bio-oil. Higher H/C ratio is favorable for the energy content, for example, fossil fuels have H/C ratio of ca. 2.

Different zeolites (H-MFI, H-FAU, and H-BEA) have been studied for the catalytic upgrading of biomass pyrolysis vapors (Perego and Bosetti, 2011). Strong acidity of the zeolite led in general to deep deoxygenation and severe coke formation (Bridgwater, 2004; Carlson et al., 2009; Thring et al., 2000; Williams and Horne, 1995). To tackle this problem, mesoporous materials with milder acidity such as SBA-15, Al-MSM-41 and Al-MSU-F have been developed (Jackson et al., 2009; Pattiya et al., 2008; Triantafyllidis et al., 2007). However, the degree of deoxygenation using these catalysts was low compared to zeolites. Alkali metals and alkaline earth metals have attracted attentions as promising catalysts for upgrading of bio-oil in recent years (Fahmi et al., 2007; Mullen and Boateng, 2008). Sooknoi et al. (2008) used Cs catalyst in combination with zeolite NaX for deoxygenation of methylesters and found that Cs plays a crucial role in decarbonylation of methylesters and when Cs was not present on the zeolite the activity of the catalyst for decarbonylation decreased. Furthermore, it was shown that non-zeolitic basic catalysts, such as MgO, had low activity for the deoxygenation of methylesters. Babich et al. (2011) studied the influence of Na<sub>2</sub>CO<sub>3</sub> on the pyrolysis of algae as biomass and found it effective for the improvement of bio-oil energy content (40% energy recovery in bio-oil). Recently, it was shown that supported Na<sub>2</sub>CO<sub>3</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, was more effective on reducing the oxygen content and enhancing the energy content of bio-oil compared to Na<sub>2</sub>CO<sub>3</sub> (Ngunyen et al., unpublished results).

In this work the effect of mesoporous amorphous silica alumina (ASA) in combination with alkali or alkaline earth metals on pyrolysis of lignocellulosic biomass is evaluated. Accordingly, ASA was selected as support and was modified with alkali metal or alkaline earth metal salts including Na, K, Cs, Mg and Ca. To the best of our knowledge such work has not been reported in literature so far. The influence of alkali-modified ASA catalysts on conversion of

pyrolysis vapors were studied and the relation between the composition of the resulting bio-oil and its properties is discussed.

## 2. Experimentals

### 2.1. Materials

Canadian pinewood with particles sizes between 100 and 300  $\mu$ m was used as biomass feed (Table 1). The other chemicals used in this study were: Na<sub>2</sub>CO<sub>3</sub> (Sigma–Aldrich, 99.5%), Ca(-NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Aldrich), K<sub>2</sub>CO<sub>3</sub> (Riedel-de Haën, 99%), CsNO<sub>3</sub> (Acros, 99.3%), Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma–Aldrich) and ASA (Si<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio 12:1; BET surface area 535 m<sup>2</sup>/g, Albemarle, The Netherlands). The amorphousness of silica alumina sample was claimed by the supplier and it was further proved by XRD analysis.

### 2.2. Proximate and ultimate analysis

Proximate analysis of the biomass sample was determined using Thermo Gravimetric Analysis (TGA) according to the following procedure: 9 mg of pinewood was heated in 50 ml min<sup>-1</sup> Ar from 25 to 200 at 10 °C min<sup>-1</sup> and kept at 200 °C for 30 min to determine weight loss due to water. Then the temperature increased to 800 °C with the same conditions and kept at 800 °C for 30 min to remove all the volatiles and to measure char content. Finally, at 800 °C, 50 ml min<sup>-1</sup> of air was introduced for 30 min. The final weight of the sample was used to calculate the ash content.

A Perkin-Elmer elemental analyzer (Thermo scientific Flash 2000), was utilized to perform ultimate analyses (C, H, and N) of the biomass and bio-oil samples. The analyzer was equipped with a column including two reactive beds, copper oxide and electrolyte copper, and the Thermal Conductivity Detector (TCD) was used for the detection of gases. The column was preheated to 900 °C. Ar and O<sub>2</sub> were used as carrier and reactive gases with flow rate of 140 and 250 ml min<sup>-1</sup>, respectively. The samples (3–4 mg in small tin cups) were inserted by a robot to the column and the weight percentage of C, H and N were calculated based on the amount of H<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub> evolved from the decomposition of the samples and using calibration curves (acetanilide used as standard for calibrating the column). Oxygen was calculated by difference.

### 2.3. Catalysts preparation

Catalysts used in this study were prepared using a dry impregnation method. First, 10 g of the ASA support (pore volume, 0.6 ml g<sup>-1</sup>) was calcined at 650 °C for 300 min in 50 ml min<sup>-1</sup> of air. Then, the desired amount of alkali or alkali earth metal precursor was dissolved in 10 ml of deionized water and loaded onto the support in two steps to give 10 wt.% of the respective metal in the final catalyst. In the first step, 6 ml of the solution was loaded onto the support by a dropper and the resulting catalyst was left at room temperature for 5 h to be dried. Then the rest of the solution was loaded onto the catalyst and it was dried at room temperature overnight and further at 120 °C for 120 min prior to calcination. Finally, each catalyst was calcined at 600 °C for 300 min in 50 ml min<sup>-1</sup> of

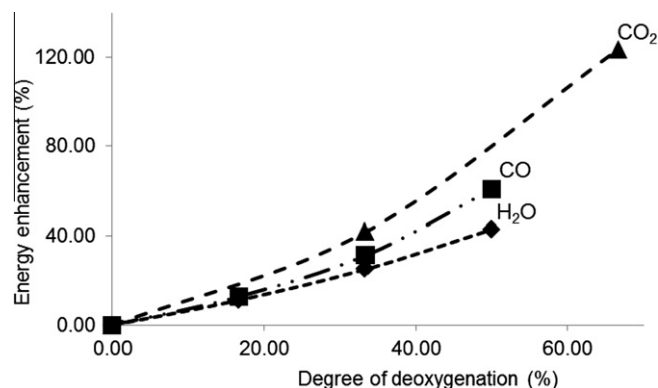


Fig. 1. Effect of deoxygenation route on the energy enhancement of biomass; energy enhancement was calculated according to following equation:  $((HHV_{product} - HHV_{biomass})/HHV_{biomass}) \times 100$ ; the data were calculated based on removal of one, two and three moles of each corresponding molecules from glucose.

Table 1  
Proximate and ultimate analysis of Canadian pine wood.

Proximate analysis (wt.%)		Ultimate analysis (wt.%) <sup>a</sup>	
Water content	3.00	C	50.15
Volatile	77.00	H	5.41
Fixed carbon	11.00	O	44.37
Ash	9.00	N	0.06

<sup>a</sup> Data were calculated on ash free basis.

air. The temperature ramp was set to  $3\text{ }^{\circ}\text{C min}^{-1}$ . The catalysts were denoted as M/ASA, where M is an alkali or alkaline metal.

Coke deposit on catalysts was measured using TGA analysis; coked catalyst was heated from 25 to  $650\text{ }^{\circ}\text{C}$  with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in  $50\text{ ml min}^{-1}$  of air and kept at the final temperature for 20 min.

The surface areas of the samples were analysed on a Thermo Finnigan surface area analyser. First, approximately 300 mg of sample was weighted and then the sample was degassed at  $300\text{ }^{\circ}\text{C}$  for 3 h to remove physisorbed water on the surface of catalyst. The specific surface areas of the samples were calculated from adsorption of nitrogen at relative pressure between 0.05 and 0.25 using Brunauer Emmett and Teller (BET) method.

#### 2.4. Pyrolysis experiments

All the catalytic pyrolysis reactions were carried out in an experimental setup (Fig. 2) consisting of a quartz tube ( $500 \times 9\text{ mm}$ ) with two separated fixed-beds: a fixed-bed of biomass which could be heated rapidly ( $1700\text{ }^{\circ}\text{C min}^{-1}$ ) to  $450\text{ }^{\circ}\text{C}$  in an Infrared oven and a fixed-bed of catalyst (bed length of 70 mm) which was also set at  $450\text{ }^{\circ}\text{C}$ . Both biomass and catalyst beds were fixed using quartz wool plugs. In order to measure the temperature rise of the biomass sample precisely, a thermocouple was placed at the center of the biomass sample using a 0.6 mm ceramic tube. The space between biomass and catalyst beds was also heated to  $450\text{ }^{\circ}\text{C}$  using a small electrical heater. Biomass vapors produced in the Infrared oven were carried through to the catalyst bed using Ar flow at  $50\text{ ml min}^{-1}$ . The vapors leaving catalyst bed passed through two sequential condensers (both at  $-45\text{ }^{\circ}\text{C}$  using a liquid nitrogen/iso-propanol mixture) where the condensable vapors (including organic components and water) were collected. The non-condensable gases (including permanent gases,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2$  and  $\text{C}_3$  gases) were collected in a gasbag. In all experiments the catalyst particles sizes were between 0.4 and 0.6 mm and were mixed with  $\alpha$ -alumina in a mass ratio of 1:1; the amount of the catalyst and biomass used were 0.75 and 1.50 g, respectively, resulting in the catalyst to biomass mass ratio of 1:2.

The yield of liquid product was calculated by the total weight difference of condensers before and after the reaction divided by the initial weight of biomass. Solid yield was also calculated using the weight difference of the quartz reactor, filled with biomass and

catalyst, after and before the pyrolysis reaction divided by the weight of initial biomass. The method used for calculations of gas yield is described in the following section.

#### 2.5. Analysis of pyrolysis products

Detection and identification of bio-oil components, collected in the condensers, were performed on an Agilent 6890N Gas Chromatograph (GC) coupled with an Agilent Inert XL Mass Spectrometry (MS) detector. A capillary column (Varian CP9154  $60\text{ m} \times 0.25\text{ mm} \times 250\text{ }\mu\text{m}$ ) was used in combination with He the carrier gas with a flow rate of  $1\text{ ml min}^{-1}$ . Bio-oil samples were diluted with acetone to a dilution factor of 5 and filtered using a  $0.25\text{ }\mu\text{m}$  PTFE filter prior to the injection. The injector port of the GC was set at  $250\text{ }^{\circ}\text{C}$  and the split ratio was 30:1. The mass spectrometer was operated in the Electron Ionization mode and the spectra were recorded from  $m/z$  of 25 to 500. Identification of compounds eluting from the GC column was done based on the retention time and the fragmentation pattern in the MS, using the NIST library (supplied by Agilent).

Gaseous products were analyzed offline using a micro GC (Varian-CP4500) equipped with two columns and a TCD. The first column (MS5A) was set at  $70\text{ }^{\circ}\text{C}$  and was used for determination of  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{CO}$  and the second column (Porapak Q) was set at  $80\text{ }^{\circ}\text{C}$  to detect  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_8$ . Both columns were calibrated for quantification of all gas components using at least two standard calibration gas mixtures and argon was used as carrier gas for both columns. The total volume of gases, which flew to the gasbag, was measured using a gas flow meter (Fig. 2). This, together with the compositions analysed by the micro GC, provide the exact volume percentage of each gas in the mixture. The ideal gas law was employed to calculate the molar amount of each gas.

Stability and molecular weight distribution of bio-oil were determined by Size Exclusion Chromatography (SEC) and according to the method by Hoekstra et al. (2011). The SEC system used was Agilent Technologies 1200 series equipped with a autosampler and a Refractive-Index Detector (RID, G1362A).

The Higher Heating Value (HHV) of bio-oil samples was estimated using the Dulong equation (Eq. 1), where C, H, and O are carbon, hydrogen and oxygen in weight percentages, respectively. Dulong formula has been used to semi-quantitatively calculate the HHV of fuels or fuel resources such as coal, biomass, pyrolysis

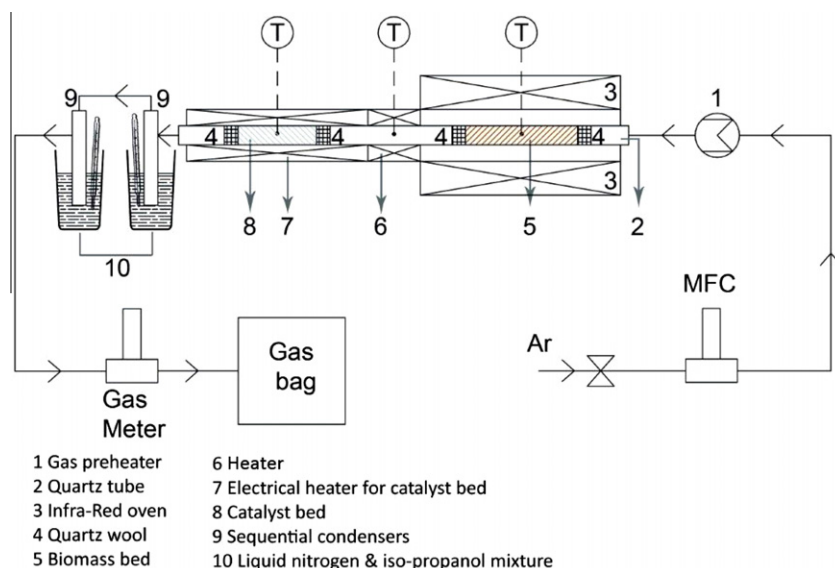


Fig. 2. Experimental set-up scheme for the *in situ* catalytic pyrolysis upgrading of biomass.



oil and biodiesel using elemental weight percentages (Buckley, 1991; Fassinou et al., 2011). Water content of bio-oil was measured using Karl-Fischer titration. Degree of deoxygenation of bio-oils was calculated using Eq. (2).

$$\text{HHV}(\text{MJ. kg}^{-1}) = (337C + 1442(H - O/8))/1000 \quad (\text{Eq. 1})$$

$$\text{Deoxygenation degree}(\%) = (1 - ([O]_{\text{bio-oil}}/[O]_{\text{biomass}})) \times 100, \text{ where } [O] \text{ is oxygen content(mass)} \quad (\text{Eq. 2})$$

All the pyrolysis experiments and analysis were duplicated and performed in random orders to obtain a good estimation of experimental errors and all the values presented are averaged. The experimental errors calculated were smaller than 5%.

### 2.6. Catalysts reproducibility and regenerability tests

The reproducibility and regenerability tests were carried out for the best-selected M/ASA catalyst (M is an alkali or an alkaline earth metal). Two batches of selected M/ASA catalyst were prepared according to the method described in Section 2.3 and were applied in the pyrolysis reaction according to the method explained in Section 2.4. The reproducibility of M/ASA catalyst was then evaluated by comparing the BET surface areas of the two catalysts and comparing the bio-oil yields obtained using each catalyst. The catalysts of each batch were denoted as M/ASA-1st-batch and M/ASA-2nd-batch for the first and the second batches, respectively. In order to test regenerability of M/ASA catalyst, the M/ASA-1st-batch catalyst was removed from the reactor after the pyrolysis reaction and was calcined in air at 600 °C for 5 h to be regenerated. This catalyst was denoted as “M/ASA-1st-batch-reg” and the BET surface area of the sample was measured. Then the regenerated catalyst was used in the pyrolysis reaction and the bio-oil yield obtained using the catalyst was also calculated. Similar to reproducibility test, the regenerability of the catalyst was also evaluated based on the BET surface area and the bio-oil yield.

## 3. Results and discussions

### 3.1. Catalytic effect on pyrolysis products yield

Detailed mass balances for the catalytic and thermal (in presence of inert  $\alpha\text{-Al}_2\text{O}_3$ ) experiments are summarized in Table 2. The solid deposited on the catalyst is denoted as heterogeneous char, which forms from re-polymerization of pyrolysis vapors and contains C, H and O. As can be seen from Table 2, the yield of residuals (homogeneous char and ash) left in Infrared oven after depolymerization of

biomass is nearly the same for all experiments, as expected. The total mass balance for all the pyrolysis reactions calculated was closed to  $90 \pm 2$ . This is mainly due to the difficulty in the collection of the small amounts of liquid product during the laboratory experiments. Moreover, for the calculation of concentrations of gases we assumed the gases to be ideal which in reality is not the case.

The yield of organics decreased for all the catalytic experiments as compared to thermal experiment. This reduction is associated with an increase in water, heterogeneous char and gas yield (Table 2) which are characteristic products of catalytic cracking reactions. Catalyst containing Cs produced the lowest amount of organic oil and resulted in the highest gas and heterogeneous char yields. The solid deposit on Na/ASA catalyst was low and a relatively high amount of organics was obtained. The least amount of water and consequently the largest organics yield was obtained using Mg/ASA indicating that this catalyst is the least selective for dehydration reactions. Water is primarily produced during depolymerization of cellulose, hemicellulose and lignin i.e., scission of glycosidic linkages in the polysaccharide units, or ether links in lignin. Water can also be further formed from catalytic deoxygenation of pyrolysis vapors (Carlson et al., 2009; DeGroot et al., 1988; Yang et al., 2007).

### 3.2. Catalytic effects on deoxygenation of pyrolysis vapors

Table 3 represents the results for the elemental analysis of the bio-oils (dry basis) produced using each catalyst, higher heating value (dry basis) of the bio-oils and overall yield of CO and CO<sub>2</sub>. K/ASA was the most active catalyst to eliminate oxygen from the pyrolysis vapors as CO<sub>2</sub> followed by Na/ASA. Mg/ASA, which showed minimal dehydration, was also not effective for decarboxylation, showing only small amounts of CO<sub>2</sub>. Cs/ASA produced the highest yield of CO.

In contrary with thermal reaction, the heating value of bio-oil increased when a catalyst was applied and this enhancement was more significant in the case of Na/ASA and K/ASA. These catalysts showed selective deoxygenation to CO<sub>2</sub>, and as suggested earlier (Section 1, Fig. 1) also gave products with the highest energy contents. Even though the degree of deoxygenation by Cs/ASA and Ca/ASA catalysts were relatively high, the resulting bio-oil energy content was lower because H<sub>2</sub>O, CO and not CO<sub>2</sub> were the main deoxygenation products.

### 3.3. The influence of the catalysts on bio-oil composition

A large number of components were detected in the liquid fraction (using GC/MS) and about 90 components matched with the NIST database at a quality level (>80%). The concentrations of these components were estimated semi-quantitatively using Total Ion Chromatogram (TIC) peak areas of the MS detector and relative response factors using fluoranthene (C<sub>16</sub>H<sub>10</sub>) as internal standard. The compounds were grouped based on chemical functionalities viz., acids (R-COOH), (substituted)-phenols, carbonyls (ketones and aldehydes), (substituted)-furans and hydrocarbons (C<sub>5</sub><sup>+</sup> aliphatic and aromatic).

Monomeric sugars and heavier phenolic compounds formed from thermal pyrolysis of holocellulose (hemicellulose and cellulose) and lignin fractions of biomass, respectively, can be cracked to lower molecular weight compounds when a catalyst is used (Carlson et al., 2009; Guo et al., 2011). Results from SEC (the figure is not included in this paper) showed that among all the catalysts, Cs/ASA resulted in a narrower range of molecular weights up to 600 g mol<sup>-1</sup> while other catalysts resulted in the wider molecular weights up to 1500 g mol<sup>-1</sup>. This implies that Cs/ASA catalyst was the most efficient catalyst for the cracking of biomass vapors.

**Table 2**

Detailed mass balance of catalytic pyrolysis reactions. Reaction conditions:  $T_{\text{pyrolysis}} = 450\text{ °C}$ ,  $T_{\text{Catalyst bed}} = 450\text{ °C}$ ,  $P = 1\text{ bar}$ ,  $\text{Air flow rate} = 50\text{ ml min}^{-1}$ .

Catalyst	Organics yield (wt.%)	Water yield <sup>1</sup> (wt.%)	Gas yield (wt.%)	Heterogeneous <sup>2</sup> char yield (wt.%)	Residual yield <sup>3</sup> (wt.%)
$\alpha$ -Alumina	42.4	19.1	10.5	0.0	17.6
Na/ASA	29.7	23.3	15.8	3.5	18.0
K/ASA	24.5	23.4	15.4	6.6	18.7
Cs/ASA	20.5	24.6	17.1	8.3	19.3
Mg/ASA	34.3	21.0	13.0	6.3	18.5
Ca/ASA	23.1	27.1	13.2	6.2	19.2

<sup>1</sup> Water yield measured by Karl-Fischer analysis; the sum of organic yield and water yield is equal to the total bio-oil yield.

<sup>2</sup> Heterogeneous char yielded on the catalyst.

<sup>3</sup> Residual is sum of char + ash.

**Table 3**  
Comparison of catalytic influences on the deoxygenation of bio-oil and higher heating value of bio-oil. Reaction conditions:  $T_{\text{pyrolysis}} = 450\text{ }^{\circ}\text{C}$ ,  $T_{\text{Catalyst bed}} = 450\text{ }^{\circ}\text{C}$ ,  $P = 1\text{ bar}$ ,  $\text{Ar}_{\text{flow rate}} = 50\text{ ml min}^{-1}$ .

Catalyst	$\text{CO}_2^a$	$\text{CO}^a$	$\text{H}_2\text{O}^a$	$\text{C}^b$	$\text{H}^b$	$\text{O}^b$	Deoxygenation degree (%)	HHV ( $\text{MJ kg}^{-1}$ )
$\alpha$ -Alumina	4.8	4.7	19.1	53.0	5.8	40.6	64.0	18.9
Na/ASA	7.4	7.2	23.3	64.6	5.3	29.5	80.9	24.1
K/ASA	7.7	6.9	23.4	63.0	5.7	30.6	82.5	24.0
Cs/ASA	6.6	10.0	24.6	59.3	4.8	35.1	84.9	20.0
Mg/ASA	5.9	6.7	21.0	53.3	6.8	39.4	73.1	20.6
Ca/ASA	7.0	5.6	27.1	61.2	4.6	33.5	85.3	21.0

<sup>a</sup> Yield (wt.%) based on the initial weight of biomass.

<sup>b</sup> Quantity of elements in dry bio-oil (wt.%); the difference of 100 and sum of H, O and C is equal to the quantity of nitrogen.

In the following sections the influence of catalysts on the cracking of holocellulose and lignin fractions of biomass and the relationships between the products thus formed and the properties that are critical in terms of bio-oil quality such as acidity, stability and energy density are discussed.

### 3.3.1. Acidity of bio-oil

Bio-oil acidity can be determined as the total acid number using potentiometric titration in which a solution of bio-oil (normally in methanol or ethanol) is titrated by a strong base such as NaOH or KOH. Based on the experimental results it was found that the total acid number of bio-oil measured by titration is closely correlated to organic acids concentration measured by GC/MS. Westerhof et al. (2011) also observed the same correlation. Phenolic compounds can also contribute to the acidity of bio-oil (phenol,  $\text{pK}_a = 10$ , acetic acid  $\text{pK}_a = 4.8$ ), but to a much lesser extent. Further, the acidity of phenolics depends on substituents, electron-withdrawing groups such as carbonyls, increase the acidity while the electron-donor substituents, such as methoxy and methyl groups, reduce the acidity via inductive and resonance effects (Wade, 2006). Accordingly, alkyl substituted phenolics would be more desirable from catalytic cracking of lignin since it has less acidity than phenol. Favorably, it has also a higher heating value (cf.  $34.2\text{ MJ kg}^{-1}$  for methyl phenol compared to  $33.11\text{ MJ kg}^{-1}$  of phenol). Therefore, total organic acids content (such as acetic acid, propanoic acid and formic acid) and the concentration of carbonyl substituted phenols (such as vanillin and 4-hydroxybenzaldehyde) were used to estimate the trend in acidity of the product when changing the catalyst (Fig. 3).

Because the yield of the carbonyl substituted phenols (Fig. 3) is low compared to the yield of carboxylic acids, acidity is apparently dominated by carboxylic acids. Among all the catalysts only K/ASA catalyst reduced the amount of acids compared to thermal run. Na/ASA catalyst made no significant changes in the content of acids. The use of the other catalysts resulted in an increase in the amount of acids and this increase was the most pronounced in the case of Cs/ASA. Acetic acid, the most abundant organic acid in bio-oil, is mostly formed from cleavage of acetyl groups in the hemicellulose fraction, mainly attached to xylose monomer (Guo et al., 2011). Deoxygenation of carboxylic acids is expected to yield  $\text{CO}_2$ . Thus, a correlation between  $\text{CO}_2$  formation and product acidity is expected; an increase in  $\text{CO}_2$  formation was observed when the bio-oil contained lower concentrations of organic acids.

Deoxygenation as  $\text{CO}_2$ , reduces acidity and enhances the energy content, as discussed earlier (Section 1, Fig. 1). Since the yield of the carbonyl-substituted phenols (Fig. 3) is low compared to the yield of carboxylic acids, deoxygenation of the latter as  $\text{CO}_2$  is more critical, as carboxylic acids cause the most acidity. Pattiya et al. (2008) assessed the catalytic influence of ZSM5, a strong solid acid catalyst with micropores, and Al-MSU-F, a mesoporous catalyst with mild acidity, on bio-oil acidity and observed that acid quantity of bio-oil increased significantly in both cases. Presence of alkali is

apparently the reason that K/ASA is effective in reducing acid components.

### 3.3.2. Stability of bio-oil

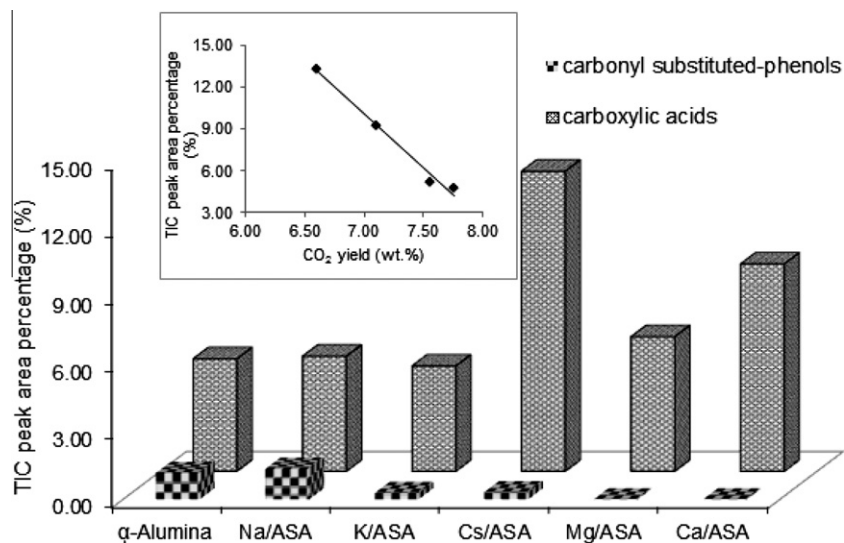
Viscosity and the molecular weight of bio-oil are known to increase by aging and significant effects already have been reported for storage for 1 week at a temperature of  $80\text{ }^{\circ}\text{C}$  (Boucher et al., 2000). Fig. 4a proves this phenomenon by comparing SEC chromatographs of a fresh bio-oil (produced from thermal pyrolysis reaction of wood) and the same bio-oil stored for one year (labeled as old bio-oil) at room temperature. It can be clearly seen from the figure that by aging, the intensity and peak area of the lower molecular weights regions decreased and the chromatograph shifted to higher molecular weight regions, reaching  $10,000\text{ g mol}^{-1}$  for the old bio-oil.

The origin of this phenomenon lies in the occurrence of chemical reactions between reactive components present in bio-oil, such as aldehydes and ketones, resulting in the formation of heavy molecules (Boucher et al., 2000; Czernik and Bridgwater, 2004; Tang et al., 2010). Examples of possible reactions are reactions of aldehydes with phenolics and aldol type condensation reactions. GC/MS analysis of the fresh bio-oil and the old bio-oil are shown in Fig. 4b (inset is chromatogram of the old bio-oil). The figure indicates that the amount of ketone, aldehydes and phenolic compounds in the bio-oil decreased tremendously by aging process (compare intensity of the peaks appeared after retention time of 10 min in the fresh and old bio-oil chromatograms). This is in agreement with the increase in bio-oil molecular weight presented in Fig. 4a. Furthermore, occurrence of condensation reactions can be proved by comparing the amount of water in the fresh bio-oil with the amount of water in the old bio-oil (24 wt.% in the fresh bio-oil vs. 38 wt.% in the old bio-oil). Therefore, based on the above premises it is expected that product oils with lower carbonyl contents are thermally more stable.

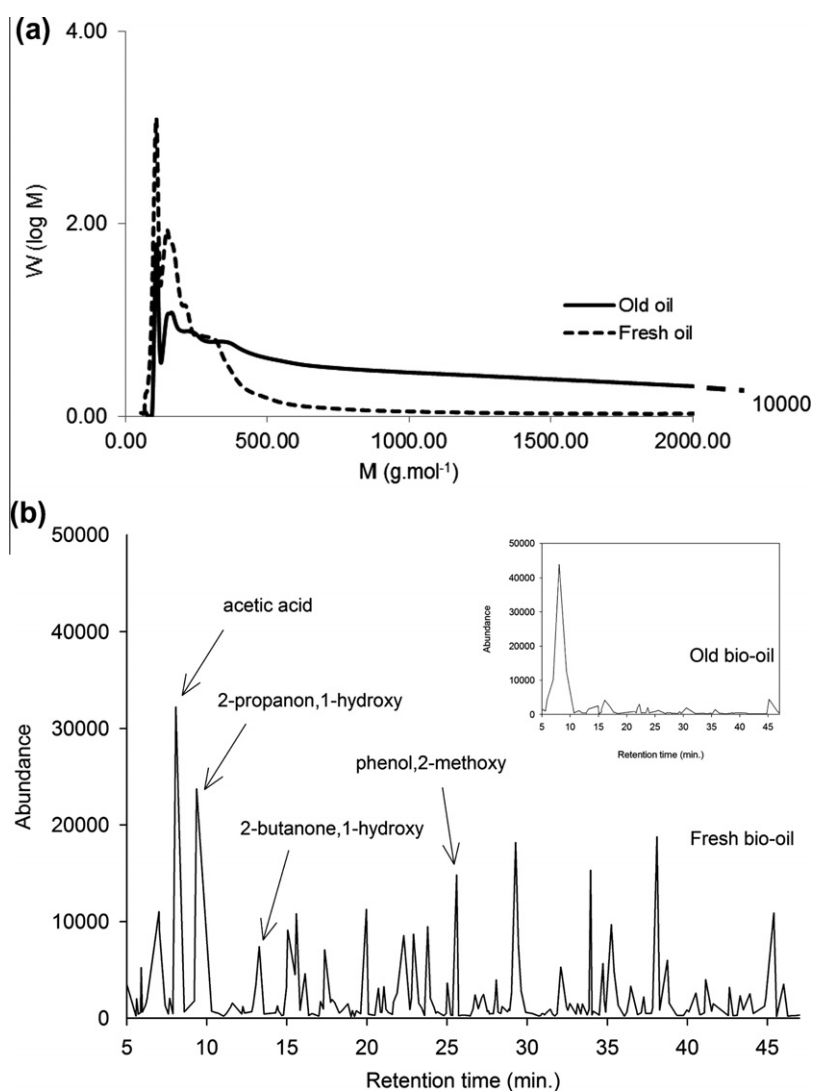
In this work, the quantity of carbonyls produced in all catalytic reactions was higher compared to the thermal (in presence of inert  $\alpha\text{-Al}_2\text{O}_3$ ) reaction (the results are not shown). Largest amounts were found with K/ASA, while the effect when using Na/ASA as the catalyst was the lowest. It is clear from this study that a higher degree of deoxygenation to lower carbonyl content, eventually via HDO, may be necessary. The results for the increase in the quantity of carbonyls are in accordance with other studies (Fahmi et al., 2007; Nowakowski and Jones, 2008; Patwardhan et al., 2010).

### 3.3.3. Energy density of bio-oil

The energy density of bio-oil is very low as compared to the energy density of conventional fuels (lower than 50%) due to the high oxygen content (typically 35–40 wt.%). However, oxygen-containing molecules such as (alkyl)-furans are desired components because of their high octane number (2,5-dimethylfuran – RON 120) and can enhance energy density of bio-oil (Czernik and Bridgwater, 2004). Lower levels of phenolic components are suggested



**Fig. 3.** Effect of the catalysts on the yield of carboxylic acids and carbonyl substituted-phenols; inset shows the Carboxylic acids – CO<sub>2</sub> yield correlation (Mg/ASA showed lower activity for deoxygenation compared to other catalysts and hence it was not included in the correlation (inset figure)).



**Fig. 4.** Increase in the molecular weight of bio-oil due to aging process and its correlation with the reduction of reactive components in bio-oil over time, shown respectively as (a) SEC chromatogram (b) GC-FID chromatogram; the high intensity peak appeared between 6 and 10 min in the old bio-oil chromatogram is due to acetic acid.

as fuel additives, as they are known to be octane increasing agents (Kleinert and Barth, 2008; Leung, 2010). Alkyl-phenols are even better because of their higher octane number. They also have higher heating values, methyl phenol having calorific value of  $34.15 \text{ MJ kg}^{-1}$ . Hydrocarbons present are the most desired components of bio-oil since they have high heating value and high octane number.

Fig. 5a compares the capability of the catalysts to form furanic compounds during catalytic cracking of biomass. In the thermal experiment, only oxygenated furans (furan with an oxygen-containing substitute e.g., furanone and furfural), were observed. Only in the case of K and Ca/ASA catalysts an appreciable increase in (alkyl-) furans was observed. Pyrolysis of xylan, a model compound of hemicellulose, in the presence of HZSM5, H- $\beta$  and USY zeolites studied by Guo et al. (2011) showed that the amount of furans decreased compared to thermal reaction. Milder acidity of the mesoporous ASA and presence of alkali metals can improve basicity therefore seems beneficial.

Phenols, formed from the pyrolysis of lignin part of the biomass (Buckley, 1991), were classified into three groups (i) phenol, (ii) alkyl substituted and (iii) substituted with oxygen-containing groups (such as C–O, OH and C=O) and are shown in Fig. 5b. The most effective catalyst on the cracking and deoxygenating of pyrolytic lignin is Cs/ASA since more than 50% of the phenolic compounds obtained using this catalyst consisted of phenol and alkylated phenols.

The catalytic effect on the quantity of desirable hydrocarbons (poly aromatic hydrocarbons were excluded) was also evaluated

by comparing the TIC peak area percentage of the total hydrocarbons detected by GC/MS. The results revealed that, all the catalysts enhanced the formation of hydrocarbons compared to the thermal reaction (nearly 0.0%) and Cs/ASA was the most effective catalyst (7.0%), followed by Na/ASA and K/ASA (3.8% and 3.0%), respectively. Mg/ASA and Ca/ASA resulted in lower amounts of hydrocarbons (1.9% and 2.0%, respectively) compared to the other catalysts. Previous studies showed that there are two possible ways for the formation of aromatic hydrocarbons from pyrolysis of biomass when a catalyst is used; (i) by mild deoxygenation of phenols through dehydration and decarbonylation reactions and (ii) from decarbonylation and decarboxylation of furans (Carlson et al., 2009; Guo et al., 2011). Based on the discussions above it seems that the increase in aromatics with K/ASA is correlated with the reduction of furans (Fig. 5a) and in the case of Cs/ASA it is correlated to the reduction of phenols (Fig. 5b). As furans are preferred over phenols, in general, as fuel additives, Cs/ASA catalyst would be more appropriate for the pyrolysis of lignocellulosic biomass. Carlson et al. (2009) used ZSM5 as an acid catalyst for pyrolysis of cellulose and they found that around 30% (mole basis) of cellulose was converted to aromatic hydrocarbons. Nevertheless, a large amount of coke (25%) was formed on the catalyst.

Among the catalysts tested in this work, Cs/ASA catalyst, in particular, is a good candidate since it had substantial influence on the cracking and deoxygenation of pyrolytic lignin and formation of aromatic hydrocarbons. Lignin is the second most abundant biopolymer in nature and it is produced in large amount as by product from pulping processes and cellulose extraction and it has no

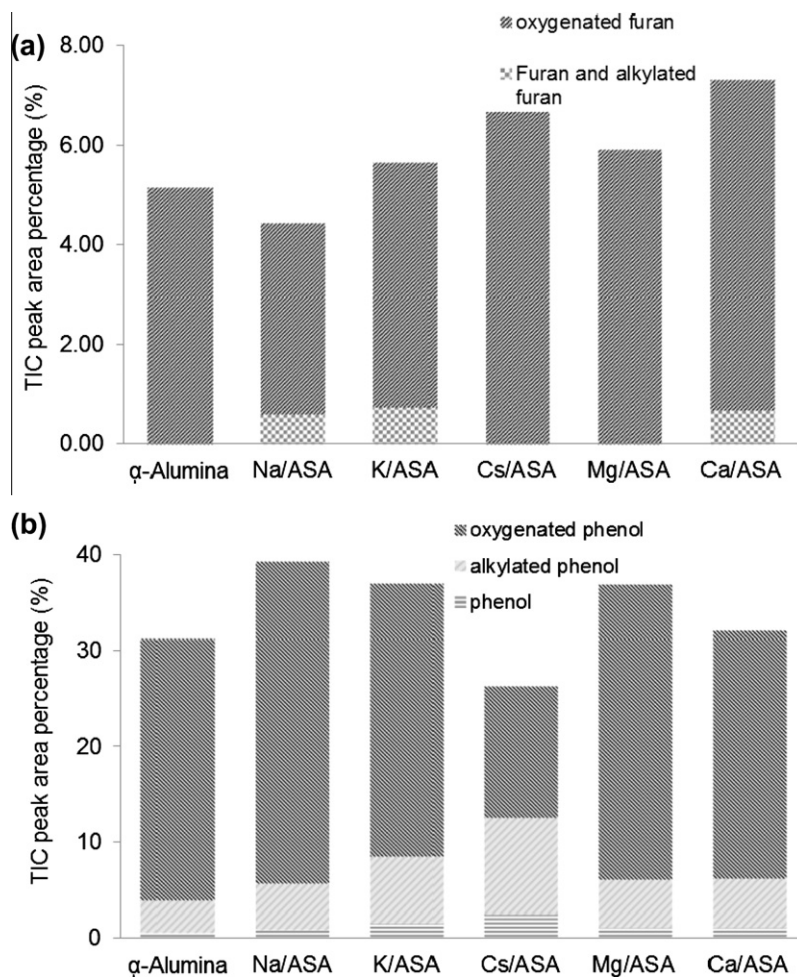


Fig. 5. Catalytic influence on the production of fuel compatible products (a) furanic compounds (b) phenolic compounds.



**Table 4**

Surface area and liquid yields of the reproduced and regenerated Cs/ASA catalysts.

Catalyst	BET surface area (m <sup>2</sup> /g)	Liquid yields (wt.%) <sup>b</sup>
Cs/ASA-1st-batch	426.6	45.1
Cs/ASA-2nd-batch	432.0	48.3
Cs/ASA-1st-batch-reg. <sup>a</sup>	381.5	45.0

<sup>a</sup> Cs/ASA-1st-batch-reg.: the Cs/ASA catalyst from 1st batch which was regenerated at 600 °C after being used in 1st cycle of the reaction.

<sup>b</sup> Reaction conditions:  $T_{\text{pyrolysis}} = 450$  °C,  $T_{\text{Catalyst bed}} = 450$  °C,  $P = 1$  bar, Arflow rate = 50 ml min<sup>-1</sup>.

competition with food chain. Therefore, it can be used as a very cheap renewable source of energy. To improve the selectivity and reactivity of Cs/ASA for lignin catalytic pyrolysis, a thorough understanding of the reaction sequences taking place is crucial. However, as shown in the introduction section, lignin pyrolysis is very complex and it is difficult to investigate the exact reaction sequences. For this reason, detailed catalytic pyrolysis studies with single model components representative of lignin structure *e.g.*, guaiacol and syringol are essential.

### 3.3.4. Reproducibility and regenerability tests of Cs/ASA catalyst

In order to use a potential catalyst in a commercial application it is important to test the reproducibility and regenerability of that catalyst. The BET surface areas of the Cs/ASA-1st-batch, Cs/ASA-2nd-batch and Cs/ASA-1st-batch-reg catalysts and the bio-oil yield obtained using each catalyst are compared in Table 4. As can be seen from Table 4, the catalysts from different batches were resulted in surface areas with very close values, which mean that the catalyst is reproducible. In addition, the bio-oil yields obtained using each catalyst are almost the same. Results from Table 4 also reveal that the BET surface area of the regenerated catalyst (Cs/ASA-1st-batch-reg) decreased slightly while the yield of bio-oil retained after using the catalyst in the pyrolysis reaction. This implies that the catalyst is also regenerable.

## 4. Conclusions

Influences of different alkali/ASA catalysts on pyrolysis of lignocellulose biomass were compared. All the alkali/ASA catalysts were effective on the deoxygenation of biomass vapors. K/ASA and Na/ASA were the most active catalysts to eliminate oxygen via decarboxylation while Cs/ASA catalyst was the most active catalyst to remove oxygen via decarbonylation. Moreover, Cs/ASA selectively converted undesired phenols to hydrocarbons, maximized the amount of required furans, and seems a proper candidate for the production of fuel compatible components from biomass, specifically from lignin fraction. Detailed structure–activity correlations of the catalyst are being established currently using simple lignin model compounds.

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## References

- Ardiyanti, A.R., Gutierrez, A., Honkela, M.L., Krause, A.O.I., Heeres, H.J., 2011. Hydrotreatment of wood-based pyrolysis oil using zirconia-supported mono- and bimetallic (Pt, Pd, Rh) catalysts. *Appl. Catal. A* 407, 56–66.
- Babich, I.V., van der Hulst, M., Lefferts, L., Moulijn, J.A., O'Connor, P., Seshan, K., 2011. Catalytic pyrolysis of microalgae to high-quality liquid bio-fuels. *Biomass Bioenergy* 35, 3199–3207.

- Boucher, M.E., Chaala, A., Pakdel, H., Roy, C., 2000. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part II: stability and ageing of bio-oil and its blends with methanol and a pyrolytic aqueous phase. *Biomass Bioenergy* 19, 351–361.
- Bridgwater, A.V., 2004. Biomass fast pyrolysis. *Therm. Sci.* 8, 21–49.
- Bridgwater, A.V., 2012. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* 38, 68–96.
- Buckley, T.J., 1991. Calculation of higher heating values of biomass materials and waste components from elemental analyses. *Resour. Conserv. Recy.* 5, 329–341.
- Carlson, T.R., Tompsett, G.A., Conner, W.C., Huber, G.W., 2009. Aromatic production from catalytic fast pyrolysis of biomass-derived feedstocks. *Top. Cat.* 52, 241–252.
- Czernik, S., Bridgwater, A.V., 2004. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* 18, 590–598.
- Fahmi, R., Bridgwater, A.V., Darvell, L.L., Jones, J.M., Yates, N., Thain, S., Donnison, I.S., 2007. The effect of alkali metals on combustion and pyrolysis of Lolium and Festuca grasses, switchgrass and willow. *Fuel* 86, 1560–1569.
- Fassinou, W.F., Steene, L.V.D., Toure, S., Martin, E., 2011. What correlation is appropriate to evaluate biodiesels and vegetable oils higher heating value (HHV)? *Fuel* 90, 3398–3403.
- Guo, X., Wang, S., Zhou, Y., Luo, Z., 2011. Catalytic pyrolysis of xylan-based hemicellulose over zeolites. *Int. J. Energy Environ.* 5, 137–142.
- Hoekstra, E., Kersten, S.R.A., Tudos, A., Meier, D., Hogendoorn, K.J.A., 2011. Possibilities and pitfalls in analyzing (upgraded) pyrolysis oil by size exclusion chromatography (SEC). *J. Anal. Appl. Pyrolysis* 91, 76–88.
- Huber, G.W., Iborra, S., Corma, A., 2006. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chem. Rev.* 106, 4044–4098.
- Jackson, M.A., Compton, D.L., Boateng, A.A., 2009. Screening heterogeneous catalysts for the pyrolysis of lignin. *J. Anal. Appl. Pyrolysis* 85, 226–230.
- Kersten, S.R.A., Vanswaaij, W.P.M., Lefferts, L., Seshan, K., 2007. Options for Catalysis in the Thermochemical Conversion of Biomass into Fuels. In: Centi, G., Van Santen, R.A. (Eds.), *Catalysis for Renewables: From Feedstock to Energy Production*, 1st ed. WILEY-VCH Verlag GmbH & Co, Darmstadt, pp. 119–145.
- Kleinert, M., Barth, T., 2008. Towards a lignocellulosic biorefinery: direct one-step conversion of lignin to hydrogen-enriched biofuel. *Energy Fuels* 22, 1371–1379.
- Leung, W.Y., 2010. Highly effective fuel additives for igniting internal combustion engines, diesel engines and jet propulsion engines. (Ed.) US Patent, Vol. US 7828,862 B2, Syn-Tech Fine Chemicals Company Limited, Ten Mum (HK), pp. 1–10.
- Mortensen, P.M., Grunwaldt, J.D., Jensen, P.A., Knudsen, K.G., Jensen, A.D., 2011. A review of catalytic upgrading of bio-oil to engine fuels. *Appl. Catal. A* 407, 1–19.
- Mullen, C.A., Boateng, A.A., 2008. Chemical composition of bio-oils produced by fast pyrolysis of two energy crops. *Energy Fuels* 22, 2104–2109.
- Nguyen, T.S., Zabeti, M., Lefferts, L., Brem, G., Seshan, K. Unpublished results. Catalytic pyrolysis upgrading of biomass vapours using Faujasite zeolite catalysts.
- Nowakowski, D.J., Jones, J.M., 2008. Uncatalysed and potassium-catalysed pyrolysis of the cell-wall constituents of biomass and their model compounds. *J. Anal. Appl. Pyrolysis* 83, 12–25.
- Pattiya, A., Titiloye, J.O., Bridgwater, A.V., 2008. Fast pyrolysis of cassava rhizome in the presence of catalysts. *J. Anal. Appl. Pyrolysis* 81, 72–79.
- Patwardhan, P.R., Satrio, J.A., Brown, R.C., Shanks, B.H., 2010. Influence of inorganic salts on the primary pyrolysis products of cellulose. *Bioresour. Technol.* 101, 4646–4655.
- Perego, C., Bosetti, A., 2011. Biomass to fuels: the role of zeolite and mesoporous materials. *Microporous Mesoporous Mater.* 144, 28–39.
- Sooknoi, T., Danuthai, T., Lobban, L.L., Mallinson, R.G., Resasco, D.E., 2008. Deoxygenation of methylesters over CsNaX. *J. Cat.* 258, 199–209.
- Tang, Z., Zhang, Y., Guo, Q., 2010. Catalytic hydrocracking of pyrolytic lignin to liquid fuel in supercritical ethanol. *Ind. Eng. Chem. Res.* 49, 2040–2046.
- Thring, R.W., Katikaneni, S.P.R., Bakhshi, N.N., 2000. The production of gasoline range hydrocarbons from Alcell lignin using HZSM-5 catalyst. *Fuel Process. Technol.* 62, 17–30.
- Triantafyllidis, K.S., Iliopoulou, E.F., Antonakou, E.V., Lappas, A.A., Wang, H., Pinnavaia, T.J., 2007. Hydrothermally stable mesoporous aluminosilicates (MSU-S) assembled from zeolite seeds as catalysts for biomass pyrolysis. *Microporous Mesoporous Mater.* 99, 132–139.
- Wade, L.G.J., 2006. *Organic Chemistry*, Sixth ed. Pearson Prentice Hall, Upper Saddle River.
- Westerhof, R.J.M., Brilman, D.W.F., Garcia-Perez, M., Wang, Z., Oudenhoven, S.R.G., Van Swaaij, W.P.M., Kersten, S.R.A., 2011. Fractional condensation of biomass pyrolysis vapors. *Energy Fuels* 25, 1817–1829.
- DeGroot, William F., Wei-Ping Pan, M.D.R., Richards, G.N., 1988. First chemical events in pyrolysis of wood. *J. Anal. Appl. Pyrolysis* 13, 221–231.
- Williams, P.T., Horne, P.A., 1995. The influence of catalyst type on the composition of upgraded biomass pyrolysis oils. *J. Anal. Appl. Pyrolysis* 31, 39–61.
- Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C., 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 86, 1781–1788.
- Zhang, H., Xiao, R., Wang, D., He, G., Shao, S., Zhang, J., Zhong, Z., 2011. Biomass fast pyrolysis in a fluidized bed reactor under N<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub> and H<sub>2</sub> atmospheres. *Bioresour. Technol.* 102, 4258–4264.